COMPLETE SPECIFICATION.

New Pigment Compositions.

We, E. I. Du Pont de Nemours and Company, a Corporation organized and existing under the laws of the State of Delaware, United States of America, of Wilmington 98, Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to new pigment compositions.

One class of pigments widely used in the prior art may be designated under the general term "flake pigments". In one of the oldest uses of such pigments, the flakes are used as reinforcing and protective pigments wherein the flake-like particles are oriented in a leafing or overlapping fashion, more or less parallel to the surface of the paint or other film.

Water-ground white mica in small sizes (200—325 mesh U.S. Standard Sieve Series) has been widely used for this purpose.

Other types of flake pigments include metal flakes, especially aluminium in various particle sizes, which have been used both for the purpose of reinforcing effects and for the essentially opaque character and shiny surfaces of such flakes, giving a film with the appearance of a metal surface.

Metal flake pigments, such as aluminium, have also found wide use because of their decorative effect, especially when mixed with other pigments, to give the well-known "metallized" appearance of many automotive finishes. Despite their desirable appearance, such metallized finishes have certain well recognized defects, including a tendency to water spot. It is also common to find that a mixture of aluminum flakes with a coloured pigment is less lightfast than the coloured pigment alone.

A third and more specialized use of certain flake pigments is to create finishes with a nacreous or pearl-like effect simulating the appearance of mother of pearl with its three dimensional effect of lustre in the depth of the film. Pigments having this effect are non-opaque with a high refractive index and vary in nature from an extract of fish scales, essentially the organic compound guanine, to flake-like crystals of certain inorganic salts, notably basic lead carbonate and lead acid phosphate. In spite of their valuable decorative properties, these products have well recognized deficiencies such as:—

1. They cannot, in general, be handled in dry form but must be stored and marketed as dispersions in the selected vehciles in which they will be used.
2. Their lightfastness does not meet the demands of many outdoor uses.
3. They are inherently very expensive to manufacture.
4. The presence of lead compounds is frowned upon in many potential uses.

This invention provides a new group of nacreous flake pigments that can be marketed in a dry, easily dispersible form, that have excellent lightfastness, are mostly non-toxic in character and relatively low in cost. They are capable of being formulated to give very desirable nacreous

effects and, moreover, within the broad group, there are many products with pronounced color in addition to their nacreous character, the colour being derived, at least in part, from the optical phenomenon of interference. Furthermore, these products may also be formulated to simulate a metallized appearance completely free from the water spotting so characteristic of finishes based on aluminum flakes. Finally, since they are flake-like in nature and chemically stable, they have the added ability to serve as reinforcing pigments.

All pigments exhibiting nacreous effects when dispersed in vehicles have certain common optical and physical characteristics that set them apart from the usual coloured pigments and white pigments of commerce. In contrast to irregularly shaped pigment particles that behave optically much like small spheres, nacreous pigments are non-opaque flake-like products in which the optical units are extremely thin flakes, at least 5 to 10 microns in major diameter and in the range of 0.1 to 3 microns in thickness. Such optcial units minimize the scattering of light and result in direct reflectance or sparkle.

Furthermore, all nacreous pigments must be transparent or translucent in character, and they must exhibit a substantial difference in refractive index from the medium in which they are dispersed. Thus, the common coating composition vehicles and plastics have refractive indices generally in the range of 1.5 to 1.6. Those pigments that have been known in the prior art as nacreous pigments have, in general, refractive indices in the range of 1.8 to 2.6. Most prior art nacreous pigments are thin flakes of a definite chemical compound. These thin flakes, in the presence of a vehicle of low refractive index, exhibit the optcial behavior of thin films including light interference and a resultant interference colour characteristic of the thickness of the film. However, the prior art flakes exhibit more or less random thicknesses, and the average effect is a blending of colours to give a nacreous or pearl-like appearance almost free of distinguishable colour.

The optical principles that explain interference colours are well known and are discussed in many textbooks of physical optics such as Robert W. Wood—"Physical Optics—3rd Edition" New York, 1936, Page 198.

According to the invention there is provided a pigment composition comprising a translucent micaceous flake substrate having on the surface thereof a translucent metal oxide layer consisting of particles, substantially all of which are less than 0.1 micron in size, of particles of one or more of the following metal oxides, namely: hydrous titanium dioxide, titanium dioxide, hydrous zirconium dioxide, zirconium dioxide, ferric oxide, chromic oxide, vanadium pentoxide, hydrous ferric oxide, hydrous chromic oxide or a mixture of two or more of these.

The new nacreous flake pigments of this invention thus comprise two parts—(1) a non-opaque flake substrate and (2) a thin adherent translucent layer of either (a) titanium or zirconium oxide with a possible second oxide as a separate layer or in admixture with the titanium or zirconium oxide, or (b) a coloured metal oxide selected from ferric oxide, chromic oxide, vanadium pentoxide and hydrous ferric and chromic oxides.

The invention also includes an article of manufacture having a pigment composition as defined above deposited thereon, a coating composition including a minor amount of such a composition and an unsupported plastic film including a minor amount of such a composition.

In the following description all mesh sizes quoted are according to United States Standard Sieve Series (meshes per inch) and all parts and percentages are by weight unless otherwise specified.

In a preferred embodiment of this invention, the substrate is a flake-like micaceous mineral, usually muscovite mica, in a selected particle size range. Flake substrates useful for the purposes of this invention are particles that have two dimensions (length and width) of similar magnitude and characteristically much greater than the third dimension. Specifically, the preferred flakes are at least 5 to 10 microns in a major dimension and 0.05 to 1.0 micron in thickness. For most pigment purposes, the upper limit in the major dimension is from 50 to 100 microns. However, for specialized uses such as in plastic articles of appreciable thickness, as linoleum, larger flakes up to as much as 1 mm. length may be used for special decorative effects. The lower limit in thickness of the mica flake is determined to a large extent by the physical strength of the flake and may be as little as 0.05 micron while an upper limit of 3.0 microns, accompanied by a correspondingly greater length and width, is fixed by the effect on the coating composition surfaces. Such flakes must also be substantially planar with a relatively smooth and light reflecting surface and must be insoluble in either water or organic solvents and inert thereto.

A satisfactory grade of mica is a water groudn white mica, frequently used as a reinforcing extender pigment in paint, all of which passes through a 200 mesh screen and 90% through a 325 mesh screen. How-

ever, for specialized purposes, it is quite possible to use flakes that are in the 140 mesh to 200 mesh range on the one hand as well as material that is considerably finer, approaching the 400 mesh size or even finer.

Another measure of particle size, more readily correlated in many ways with the application of the subsequent metal oxide film to the surface, is the specific surface area as measured by gas adsorption using the well-known B.E.T. method described by Emmet in "Advances in Colloid Science", Vol. 1, New York, Interscience Publishers, Inc., 1942, pp. 1—35. This function has been found to vary appreciably from batch to batch of nominally similar sized micas. Mica with a surface area of about 3 square meters per gram and with a reasonably uniform particle size is a particularly suitable form. However, products of acceptable properties may be obtained from samples of mica with widely differing surface areas provided appropriate adjustments are made in the amount of metal oxide applied to form the transparent layers thereon so that the use of metal oxide per unit of surface area is appropriately controlled. No arbitrary limits on surface area can be established, but a range from 2 sq. meters per gram to 7 sq. meters per gram will encompass the products most likely to be desired.

In addition to the preferred muscovite or white mica, other forms of mica such as biotite, phlogopite, the related vermiculite, and various synthetic micas, may be used as substrates in this invention. To obtain these products in the desired particle size ranges, it is preferred that they, also, be water ground. The introduction of agents to facilitate exfoliation or the introduction of other inert coatings that do not alter the refractive index of the mica nor its receptivity to the subsequently applied translucent layer of oxide is contemplated as being within the scope of this invention. The inherent colour of some of these micas influences the colour of the final products, but the interference colours of the layers deposited will still be present.

The preferred materials of the thin translucent layer of metal oxide deposited upon the mica substrate are iron (III) oxide, chromium (III) oxide, vanadium (V) oxide, the hydrous oxides of iron (III) and chromium (III) and an oxide of tetravalent titanium such as TiO_2.

The layers of metal oxides, in the hydrous forms (the hydrous vanadium oxide being a vanadium (IV) oxide) are conveniently deposited upon mica substrates by suspending the mica in acidic solutions of the appropriate metal salts

and bringing about a carefully controlled hydrolysis at such a rate that the mica flakes are able to function as nuclei for the formation of hydrous oxide layer on their surfaces. The exact physical conditions to bring about this slow formation of the hydrous oxide vary according to the metals involved.

When the metal oxide deposited in an oxide of tetravalent titanium, such as TiO_2, the hydrous oxide layer is conveniently deposited upon a mica substrate by suspending the mica in a dilute, strongly acidic solution of titanyl sulphate at ambient temperature and then hydrolyzing the titanyl sulphate solution by rapidly heating to 90—100° C. and maintaining at that temperature for 2—3 hours so that the hydrous titanium dioxide as formed is continuously deposited on the mica with a minimum of formation of free hydrous titanium dioxide. Alternatively, the mica may be suspended in hot water to which is then rapidly added a strongly acidic concentrated titanyl sulphate solution, after which hydrolysis and deposition of the hydrous titanium dioxide on the mica are brought about by continued heating at the boil until hydrolysis is complete. The choice between these methods is a matter of convenience.

Upon isolation of the resulting pigments by nitration and drying, there are obtained nacreous powders exhibiting brilliant interference colours when disperesed in a vehicle, the predominating colours depending (at least in part) upon the thickness of the hydrous oxide film.

The colour of the products obtained in this manner is rather subtle and is most readily observed when a film containing these new nacreous pigments is observed over a dark background. In addition to the predominant interference colour, substantially all of these products show a brilliant iridescence or a multicoloured sparkle when observed at the specular angle under bright illumination, as in sunshine. This combination of iridescence on a background of a predominating colour is an outstanding characteristic of the new products.

The new products containing hydrous TiO_2 on mica, as directly prepared by the hydrolysis of a titanyl sulphate solution in the presence of mica, although very beautiful in colour effects and useful for some purposes where not generally exposed to light, are quite photosensitive, showing marked changes in pigmented compositions containing them on exposure to light. Consequently, they require stabilization in this property for their most effective uses. This photosensitivity is believed to derive in part from either one

of two causes. On the one hand, dry hydrous TiO_2 invariably contains an appreciable amount of acidic impurities that cannot be removed by the usual tech-
5 niques of isolation of the pigment. Partial stabilization to sensitivity from this cause can be brought about by the deposition of certain other metal oxides, particularly hydrous alumina or hydrous
10 chromic oxide, upon the layer before final drying. More effective stabilization is, however, brought about by calcination at temperatures in the range of 700—1000° C., preferably in the 900—1000° C. range.
15 Products obtained by calcination in these temperatures ranges retain their brilliant interference colours to a large extent, although the predominant colours shift slightly in the direction that indicates a
20 reduction in the thickness of the layer of oxide, as would be expected by the driving out of certain impurities, including water and residual acid.

It is well known in the art that certain
25 impurities have a profound effect on light sensitivity of titanium dioxide. This effect is also found in the TiO_2 pigments of this invention. For instance, very small amounts of iron that may be introduced
30 through the use of impure raw materials or by migration from the mica during calcination are found to cause light sensitivity to increase. On the other hand, certain impurities may be deliberately intro-
35 duced by the proper selection of ram materials or the addition of appropriate salts to the titanyl sulphate solution to bring about remarkable improvements in reducing photosensitivity. Compounds of an-
40 timony, cobalt, chromium, tungsten, molybdenum, and even iron when used in substantial amounts, serve in this way. An especially valuable procedure is to add small amounts of an antimony compound,
45 for instance, antimony oxide (in the range of 0.5 to 5%, preferably about 2%, based on titanium dioxide present) prior to the calcination. In any case, small amounts of a second metal oxide, not exceeding 20%
50 by weight of the titanium oxide, may be included in the titanium oxide layer, either as an impurity or by deliberate coprecipitation.

An alternative procedure for depositing
55 the film of titanium dioxide involves the exposure of hot (600° C.) flakes of mica to the vapor of an organic titanate ester such as tetraisopropyl titanate in the absence of air or water vapor, and prefer-
60 ably in a vacuum. Likewise, other water-soluble salts of titanium may be used in the hydrolysis procedure. Thus, in particular titanium oxychloride can be used, as can certain water-soluble titanium

esters such titanium acetyl acetonate and 65 triethanolamine titanate.

Furthermore, a zirconium dioxide coating can be used in place of the titanium dioxide coating. It may be applied in a similar manner, and in similar amounts, by 70 the hydrolysis of a solution of a suitable zirconium salt (zirconium oxychloride or zirconium sulphate, for instance) in the presence of mica. It is a peculiarity of hydrous zirconium oxide that it has a 75 significantly lower refractive index than hydrous titanium oxide so that the products containing the simple layers of hydrous zirconium oxide are appreciably less nacreous in character than products 80 containing titanium oxide. However, upon calcination, a pronounced nacreous character is developed.

When the layer is iron oxide it is preferred that a substantial amount of acetate 85 ion be added to a solution of a ferric salt and to bring about the hydrolysis by a cautious heating of the resulting solutions.

On the other hand, other buffer salts are preferred in the preparation of the chromic 90 and vanadium oxides, which may be done without heating by the addition of a solution of a suitable buffer salt at room temperature, the buffer being so selected that it brings about the desired pH for hydrous 95 oxide formation at a relatively slow rate. Such a process may also be used in depositing hydrous iron oxide on mica. A preferred agent to be used in this case is borax $(Na_2B_4O_7 10H_2O)$. It is preferred to 100 add the borax in small increments so that the pH is maintained in the desired range as more fully set forth in the examples below.

The specific metal salts chosen to pre- 105 pare the chromium, vanadium and iron oxide products of this invention are not critical as to the anion present, the choice being generally dictated by availability. In the precipitation of an iron (III) oxide, 110 it is common to work with $FeCl_3$ as an available crystalline material. However, it is equally feasible to use a ferric sulphate solution that might be obtained for instance by oxidation of a solution of ferrous 115 sulphate (copperas). Other water soluble iron (III) salts, as available, can also be used.

In the choice of a chromium salt, it is common to use a chromic sulphate solu- 120 tion obtained by reduction of the readily available sodium or potassium dichromate solutions. Another commonly available salt is chromic chloride.

A commonly available salt is vanadyl 125 sulphate $(VOSO_4)$, a tetravalent vanadium derivative. Generally speaking, the simple vanadium salts are decomposed to the

vanadyl derivatives in water so the latter must be used.

The stable water solutions of these chromium, vanadium and iron salts are strongly acidic in character and hydrous oxides are precipitated when the acidity is neutralized. For the purposes of this invention, wherein the oxide is laid down as a layer on the mica flakes, it is necessary that the precipitation of the hydrous oxide be relatively slow. This is conveniently achieved by the introduction of an acid accepting buffer salt of which sodium acetate and sodium tetraborate are preferred, though any other buffer salt acting in the proper pH range, say 4 to 7, may be used.

The concentration of the metal salt solutions may vary over a wide range, say, from as much as 20% down to 2% with a preference in the range of 2 to 10%.

The amount of salt solution in relation to the mica is significant only as the means of controlling the amount of metal oxide deposited. To obtain acceptable nacreous pigments, the amount of chromium, vanadium, or iron oxide should be at least 10% of the weight of the pigment and may range upward to 30% or even 40%. Generally however, the preferred amounts of oxide deposited will be in the range of 10—30% of the pigment. The actual amount of metal salt used in the solution may often exceed the calculated amount because it is sometimes difficult to obtain complete exhaustion of the solutions in the precipitation step, within the pH range dictated by the buffer salts used. However, more drastic increase of pH by adding stronger alkaline agents is undesirable as possibly precipitating free metal oxide.

These pigments can be isolated from the reaction mixture by conventional means, conveniently by filtering, washing free of soluble salts and drying at any desired temperature, say 80° C. Products so obtained are valuable pigments, but they may sometimes be improved in stability and altered somewhat in colour by calcination in air at temperatures up to 500° C. (preferably 300—400° C.) for vanadium pentoxide (V_2O_5 melts at 690° C.) up to 700° C. for chromic oxide and up to 800° C. for ferric oxide.

A second layer of metal oxides may be deposited on top of, or intermingled with, a titanium oxide or zirconium oxide layer. The second layer may comprise one of the oxides which are colourless in the form of particles less than 0.1 micron in size such as alumina, zirconium oxide, zinc oxide, tin oxide, antimony oxide or even a second layer of titanium oxide. Such oxides are herein referred to as colourless oxides. On the other hand, it may include oxides which have inherent colour such as iron oxide, nickel oxide, cobalt oxide, copper oxide, or chromium oxide. If desired, hydrated forms of these oxides may be used. This second layer of oxide obviously alters the thickness of the total oxide layer, and thus contributes to the interference effect. It may also contribute inherent colour of its own, together with the interference colour, giving largely unpredictable tinctorial effects of great interest.

When such a second metal oxide is used, it may be deposited upon either a hydrous titanium or zirconium oxide layer or upon the corresponding calcined layer, or it may be deposited simultaneously with the titanium or zirconium oxide layer as by adding an appropriate metal salt to the titanyl sulphate or zirconium oxychloride or sulphate solution. In general, the second oxide is deposited in a lesser amount than either the titanium or zirconium oxide, preferably not more than 20% of this amount. One of the most outstanding results from the deposition of such a second metal oxide is a marked stabilization of the photosensitivity of the initial hydrous TiO_2 layer. Alumina hydrate lends itself admirably for this purpose. This material has a relatively low refractive index, and it produces stabilization with a relatively minor effect on the colour of the interference. It is most effectively deposed as a second layer by thermal hydrolysis from a buffered solution such as aluminum acetate.

Other oxides that may be deposited as a second layer include the following:—

1. Zinc oxide (ZnO) may be deposited by thermal hydrolysis of an ammoniacal zinc complex solution such as tetrammine zinc sulphate. When such a combined layer of hydrous TiO_2 and ZnO is calcined, the resulting layer exhibits the X-ray pattern of rutile TiO_2 whereas the single layers of TiO_2 show anatase TiO_2. In general, this variation appears to have a minor effect on the properties of the coated flakes.

2. Zirconium oxide (ZrO_2) may be deposited as the hydrous oxide on top of hydrous TiO_2 by the thermal hydrolysis of a solution of zirconium oxychloride, for instance. It improves the stability to light and has a minor effect on the colour. On calcination of the combined layers, however, there is an increase in refractive index that results in a colour effect which would be expected from a thicker layer.

3. An iron oxide layer (Fe_2O_3) may be deposited by the thermal hydrolysis of a solution of, for instance, ferric acetate. The resulting product, prior to calcination, is a brilliant gold flake pigment of pronounced colour that varies with the thickness of

the combined layers and is accompanied by an iridescent sparkle. Such pigments impart a pronounced two-tone effect to compositions containing them. On calcination, there is a colour change toward the red, in line with the known behaviour of iron oxides, but the nacreous effect is retained.

4. Nickel oxide is readily deposited on a hydrous TiO_2-coated mica by the thermal hydrolysis of a nickel tetrammine sulphate solution, for instance. The colour effects in this case after calcination, as shown in Example XV are quite unexpected.

Nickel oxide may also be deposited by thermal hydrolysis of a nickel acetate solution.

5. Cobalt oxide is readily deposited by the thermal hydrolysis of a cobalt acetate solution.

6. Some of the most unexpected effects are obtained with chromium oxide (Cr_2O_3). It is deposited readily by the thermal hydrolysis resulting from the volatilization of ammonia from a solution in water of a hexammine chromium (III) derivative or by the thermal hydrolysis of a chromium salt solution, buffered with borax. A very thin layer (1% to 2% of Cr_2O_3) deposited on a hydrous TiO_2 layer has resulted in marked stabilization of the photo sensitivity with very little effect on the colour of the pigment. Moreover, this thin layer of chromium oxide seems to stabilize the colour on calcination so that such products are improved both in colour and in stability to light over untreated products.

If, on the other hand, a large amount of Cr_2O_3 (5—15%) is deposited, for instance, on top of a hydrous TiO_2 with a gold interference colour and the resulting flake pigment calcined, the final product is an attractive golden nacreous pigment with an irridescent sparkle that imparts an interesting two-tone effect to compositions pigment therewith.

The above illustration with chromium oxide points to the importance of variations in the thickness of the successive layers in multilayer coatings. The amount of titanium oxide or zirconium oxide in the initial layer may vary over the whole range shown for the single layer. The resulting colours will significantly affect the properties of the final products. In like manner, the second layer may be varied in thickness by controlling the amount of reagent used and the conditions of deposition. The thickness of the second layer contributes to the interference colour in the expected manner, subject to variations in the refractive indices. The invention contemplates ranges in the individual layers of the multilayer coating comparable to those shown for TiO_2 alone.

The deposition of successive layers of metal oxides can be extended beyond two successive layers and the invention includes such multilayer coatings. It is also contemplated that thick layers of titanium oxide may be deposited in a single step or may be deposited in successive steps with or without a calcination step between.

The titanyl sulphate solution used in the preferred processes for the deposit of TiO_2 may be obtained in any convenient manner. A relatively pure titanyl sulphate may be obtained by dissolving in sulphuric acid a hydrous titanium oxide precipitate commonly obtained as an intermediate in the preparation of TiO_2 pigment. However, it has been found that such highly pure solutions are not necessary and that equivalent results can be obtained by using a conventional titanyl sulphate concentrate prepared from the ore and containing a small amount of iron maintained in the divalent state by the presence of a small amount of trivalent titanium in the strongly acid solution. Thus, the concentration of the titanyl sulphate in the aqueous solution may vary over a range, preferably from 2 parts (calculated as TiO_2) to 20 parts per 100 parts of solution. Regardless of the concentration, it is necessary that there be sufficient free acid in the solution at all times to exceed that necessary to convert all of the titanium oxide to $TiOSO_4$. This is necessary to prevent precipitation of a hydrous titanium oxide at room temperature, but there should not be so much acid present that hydrolysis is excessively repressed at elevated temperatures. The "Factor of Acidity" (F.A.) is frequently used as a parameter in the titanium dioxide art to define this relation where

$$FA = \frac{100 \ (\text{total acid—combined acid})}{\text{Combined acid (TiOSO}_4)}.$$

In the examples below, FA values of about 80 for a concentrated titanyl sulphate solution and about 220 for a more dilute solution are shown. Values in the range of 50 to 300 are preferred. The desired conditions will obviously vary with concentrations of reactants and temperature and, within a broad range, the conditions may be readily determined by the skilled worker. In general, the preferred FA values are within the range considered optimum for the preparation of pigment-grade TiO_2.

Regardless of the source of the titanyl sulphate and regardless of the concentration in the starting material, the concentration of the titanium salt in the solution in which the mica is suspended at the

point of hydrolysis is more dilute by a factor of at least 2 or 3 than is preferred for TiO_2 pigment. For the best results, this concentration of titanium salt (calculated as TiO_2) in the solution at the point of precipitation should be at least about 2 parts and should not exceed about 7 parts per 100 parts of solution.

The amount of the titanium (or zirconium) salt used in relation to the mica may vary over a wide range and is significant only as a control on the thickness of the ultimate oxide coating. In general, the usage, calculated at TiO_2 or ZrO_2, should be in the range of 10 parts per 100 parts of mica (10% by weight) up to as much as 200 parts per 100 parts of mica (66% by weight) with a preferred range for TiO_2 of 15 to 80 parts per 100 parts of mica (about 15—40% by weight of TiO_2). This is, of course, reflected in the thickness of the layer deposited and the resulting interference colour. It has been found that when the amount of TiO_2 is in the range of 10—26% by weight of the product, a silver-coloured pigment is usually obtained; in the range of 26—40%, the pigment is golden in colour; and in the range of 40—50%, the colour of the pigment varies from red to blue to green as the thickness of the metal oxide layer is increased. In the range of 50—60%, higher order interference colours are obtained. Other parameters have also been used in this invention to correlate thickness of film with interefernce colour. For example, a convenient measure of the thickness of the layer is the weight of TiO_2 deposited per unit area of mica surface (conveniently expressed as milligrams per square meter of mica surface) and this may vary from 50 mg. of TiO_2 to 600 mg. of TiO_2 per square meter of surface. In the upper portions of this range, the observed colours are higher order interference colours. The relation between the weight of TiO_2 per square meter and the colour varies somewhat between uncalcined and calcined products. However, within broad limits, the following table sets forth the correlation between the observed interference colours and the measured TiO_2 weight per square meter of mica surface. Since colours vary continuously over the spectrum, it is obvious that the ranges merge at the dividing points. Pigments having 50—280 milligrams of TiO_2 per square meter of mica surface exhibit first order interference colours, and they are preferred materials.

Colour			Mg. TiO_2 per square meter
Silver	...	...	50 to 100
Gold	...	...	100 to 180
Red	...	...	180 to 220
Violet	...	...	220 to 240
Blue	...	...	240 to 260
Green	...	...	260 to 280
2nd Order Gold		...	280 to 350

The weight of ZrO_2 per square meter will be larger than these figures because of the higher density, but the same general principles apply.

Another means for measurement of the thickness of the TiO_2 layer in relation to the colour, which depends upon direct measurement and not upon prior knowledge of the nature of the mica or the TiO_2 coating, is derived from the wave lengths of the interference bands.

In the following table, the optical path has been calculated from measurements of interefernce bands exhibited by typical products of known composition. Where possible, interference bands, either maxima or minima, falling in the visible portion of the spectrum have been used for the calculation. The silver flakes, however, have no interference bands in the visible spectrum and there is considerable uncertainty about the exact position of the interference band in the ultraviolet because of an absorption band of TiO_2 in the same region. Measurements of thickness are in millimicrons. Weight of TiO_2 per square meter is in milligrams, and they are based on direct measurements.

Colour			Optical Path (in millimicrons)	Geometric Thickness (in millimicrons)	TiO$_2$ per Square Meter (in milligrams)
Silver	...	...	96 (est.)	35 (est.)	85
Pale Gold		...	150	59	145
Gold	...	...	175	71	163
Red	...	...	250	95	186
Violet	...	...	297	117	231
Blue	...	...	325	129	250
Green	...	...	358	145	275
2nd Order Gold	...	...	412	161	320
2nd Order Violet	...	...	487	194	385

From these illustrative data, it is apparent that products of technical merit are found throughout a range of 30 to 200 millimicrons in the calculated geometric thickness of the oxide layer. It has been found in other studies that a broader range of 20 millimicrons to 250 millimicrons is also useful with the range of 20—155 millimicrons for the first order interference colours preferred.

The following table gives the colour obtained within various ranges of thickness.

Colour			Geometric Thickness Range (in millimicrons)
Silver	...	...	20—40
Pale Gold	...	...	40—90
Gold	...	...	
Red	...	...	90—110
Violet	...	...	110—120
Blue	...	...	120—135
Green	...	...	135—155
2nd Order Gold	...	...	155—175
2nd Order Violet	...	...	175—200

The thickness of a ZrO$_2$ layer may vary from the figures given above, since ZrO$_2$ has a slightly lower refractive index.

The isolation of the TiO$_2$ pigments of this invention by filtering, washing, and drying is entirely conventional. However, it is well known that a certain amount of sulphate ion is very tenaciously held by a hydrous titanium dioxide precipitate, and it is sometimes desirable to promote the more complete removal of this sulphate by washing with a dilute alkaline solution such as dilute ammonium hydroxide, either on the funnel or by re-slurrying in such a solution, followed by filtering and washing again.

The new compositions give a hitherto unknown family of coloured nacreous flake pigments that are relatively free from random scattering of light and that derive their colour solely from the optical phenomenon of interference when the layer is of a colourless titanium or zirconium oxide. When an additional adherent, translucent layer of a second metal oxide which may in itself be coloured, is deposited on, or intermingled with, the titanium oxide (or zirconium oxide) coated flakes, new products with an enhancement of colour and improvements in other properties are obtained. The use of coloured metal oxides of iron (III) oxide, chromium (III) oxide, vanadium (V) oxide and the hydrous oxides of iron (III) and chromium (III) gives a hitherto unknown family of coloured nacreous flake pigments that are likewise relatively free from random scattering of light and that exhibit both the inherent colour of the metal oxide and a reflex colour derived from the optical phenomenon of interference. When dispersed in a conventional manner as pigments in various systems the compositions exhibit novel colour effects that include the inherent colour of the metal oxide and superimposed thereon a brilliant nacreous lustre. When viewed at the specular angle under bright illumination, as in sunlight, they exhibit a striking irridescent sparkle on a background of a predominating colour. When the coatings are all of colourless oxides, the observed colour is solely the result of optical interference and varies from a silver pearl through gold and red to blue and green as the thickness of the combined oxide layers increases. When a coloured oxide is coated onto a titanium or zirconium oxide layer, both the inherent colour of the second oxide and the interference colour of the combined layers may

be observed as a variety of spectacular effects.

The hydrous iron oxide coatings of this invention are golden yellow in colour, changing to a brown and ultimately to red on calcination. Hydrous chromic oxide coatings are greenish changing to lighter green on calcination. The hydrous oxide treated products containing vanadium are brownish grey changing to a brilliant light yellow on calcination at 300—400° C.

A very unexpected aspect of this invention is the limited range of only three coloured metal oxides (chromium, vanadium and iron) which can be deposited alone as layers directly on mica flakes and be retained in the particle size range required to give a nacreous character to the products. It is shown that many metal oxides can be deposited on mica previously treated with a layer of titanium or zirconium dioxides. However, it was wholly unexpected to find that, of these oxides, only iron (III), chromium (III), and vanadium (V) oxides can be used directly on the mica to produce interference effects.

When a coloured oxide is present, in addition to the inherent colour of the oxide, the new pigments exhibit interference colours, frequently called reflex colours. These are best observed under certain specific conditions, and generally, the powders in bulk show only the colours of the metal oxides. If the powder is spread in a thin layer such as by rubbing between the fingers and observed in bright sunlight, it may show a pronounced sparkle with evidence of the reflex colour and if it is mixed with water on a black surface, the interference colour and sparkle immediately become visible.

When dispersed in coating composition vehicles and plastics, the reflex colour is best observed at the specular angle under bright illumination as in the sunshine. Since this colour generally differs from the inherent colour of the oxide, spectacular two-tone effects are often obtained.

With regard to the iron, chromium and vanadium oxides, the interference colour is a function of the thickness of the oxide film following the rules set forth above for titanium dioxide. Another measure is the actual weight per cent of the metal oxide based on the weight of the final pigment. This may vary from 10% to 40%, preferably 10% to 30%. With the smaller amounts of metal oxide, say from 10% to about 20%, the reflex colours are generally of a silvery nature becoming golden as the amount increases beyond about 20%. There is no arbitrary upper limit on the amount of metal oxides which may be deposited, but practical operation indicates that amounts in excess of about 30%

are difficult to deposit and that about 40% is the practical limit.

It appears that one of the critical features distinguishing the new products from the pigments of the prior art lies in the character of the metal oxide deposited on the mica flakes. Examination of such flakes, both before and after calcination, in the electron microscope, suggests that the hydrous oxide layers have particles so small as to be very poorly resolved in the electron microscope. They are not completely non-crystalline because they have distinguishable X-ray diffraction patterns and there is some evidence of very small particles of about 0.01 micron in size, but these particles do not appear to have sharp edges and tend to be irregular in size and shape. Upon calcination, a definite crystalline pattern becomes evident but, for products that are nacreous in character, the crystallites are extremely small and densely packed so that the optical character is that of a film.

Measurement of the TiO_2 particles shows a maximum particle size of 0.1 micron for any calcination temperature below 1000° C., the preferred calcination temperature being 700 to 1000° C. At higher temperatures some larger particles appear and when the particles of TiO_2 or other oxide exceed 0.1 micron in diameter the interference colours and the nacreous character of the product are no longer apparent. Such products exhibit the light-scattering properties of conventional TiO_2 or other pigments.

Measurement of the chromium, vanadium and iron oxide particles also shows a maximum particle size of 0.1 micron. However, there appear to be temperatures above which the particles grow to sizes substantially greater than 0.1 micron and when this occurs the nacreous character disappears. The maximum permissible temperatures differ for the three oxides being 800° C. for iron oxide, 700° C. for chromium oxide, and 500° C. for vanadium oxide. Such larger particles exhibit the light-scattering properties of conventional metal oxide pigments.

In discussing the properties of these new pigments, emphasis has been placed on compositions in which they are used alone. However, they may be used in mixtures with other pigments. With black pigments such as carbon black, there is frequently some enhancement of the effect of the reflex colour. In mixtures with conventional coloured pigments of compatible hues, the nacreous character, and frequently the sparkle as well, are retained while the effect on the colour is ofen unpredictable. Many combinations have an effect similar

to that of aluminum flakes without many of the disadvantages thereof.

When the new flakes are used in admixtures with conventional pigments of high hiding power, such as pigmentary TiO₂ for instance, a pronounced nacreous, or pearl-like, character is quite evident even with as much as 25 to 50% of TiO₂, but the irridescent sparkle may be very much diminished. Nevertheless, such mixtures offer attractive possibilities.

An outstanding property of the new flake pigments is their remarkable ease of dispersibility in coating composition vehicles. It has been considered necessary with substantially all pigments known to the art to subject them to considerable grinding action for the necessary degree of dispersion required in formulating high quality paints and enamels. Metal oxide pigments generally require substantial grinding to give acceptable enamels. Mica also requires considerable work on the system for good dispersion. It is, therefore, totally unexpected to find that the new pigments, whether calcined or not, can be dispersed in a great variety of vehicles by simple vigorous agitation. Additional grinding shows little, if any, advantage and can be easily carried to the point where the flakes are broken with an undesirable effect on the colour obtained.

These new pigments have their principal value as ingredients of compositions such as paints, printing inks, plastic films and rubber articles, to which they impart colour and other decorative effects and often exert a profound influence on the durability of such compositions on exposure to the elements. When the colour and decorative properties of pigments are spoken of, it is generally understood that reference is being made to compositions containing the pigments. The following formulations are typical of this invention.

FORMULATION A.

Unsupported Film of Cellulose Acetate.

1.0 Part of pigment is added to 20 parts of a cellulose acetate solution containing 16.7% cellulose acetate in acetone. The mixture is stirred until thoroughly mixed. A glass plate is prepared for stripping a film therefrom by coating the clean plate with a silicone stopcock grease and then wiping thoroughly with a dry cloth. The lacquer is spread on the glass plate and drawn down to a wet film thickness of about 0.16 mm. After the solvent has evaporated, the film is stripped from the plate and observed on the smooth side. Such films are conveniently used for light-fastness tests in a "Fade-Ometer" (Registered Trade Mark).

FORMULATION B.

2.5 parts pigment.
17.9 parts mixed acrylic ester polymer (Acryloid A 101—Rohm and Haas).
7.7 parts butyl benzyl phthalate.
20.0 parts monoacetate of ethylene glycol monoethyl ether.
56.9 parts methyl ethyl ketone.
50.0 parts toluene.

The pigment is dispersed by vigorous stirring with the resin and plasticizer together with a portion of the solvents for about 15 minutes; the remainder of the solvents is then added and the mixing continued until uniform. Exhibits are prepared by spraying onto primed panels and, after drying, baking at 80—85° C. for 20 minutes. Alternatively, as a quick testing method, films of this lacquer may be spread to uniform thickness with a "doctor blade" and observed after air drying.

FORMULATION C.

Baked Alkyd Enamel.

2.5 parts pigment.
29.2 parts non-oxidizing coconut oil — modified alkyd resin solution (60% solids).
13.6 parts modified melamine formaldehyde resin (55% solids).
15.0 parts aromatic hydrocarbon solvent.
19.0 parts aliphatic hydrocarbon solvent.

The pigment is added to the mixed resin solutions with a part of the solvent and dispersed by high speed stirring for about 15 minutes after which the remainder of the solvent is stirred in. The resulting enamel is sprayed onto a primed metal panel and baked one half hour at about 120° C. Films of uniform thickness may also be applied with a "doctor blade".

FORMULATION D.

Vinyl Plastic Film.

3 parts pigment.
100 parts vinyl chloride polymer.
40 parts dioctyl phthalate.
10 parts polyester resin.
3 parts stabilizer (barium-cadmium-zinc phosphite).
0.25 parts stearic acid.

The pigment is added to the mixture of ingredients and the whole mixture is processed on a two-roll mill, heated to 155° C., until uniform. It is finally taken from the mill as a sheet of any desired thickness which may be observed as obtained or may be press polished in a suitable heated press.

These compositions are all conventional and may be modified in well-known ways or may be replaced by equally conventional

compositions including cellulose nitrate lacquers, linseed or other oleoresinous varnishes, linoleum compositions, rubber and polyethylene resins.

In all cases, the observed colour can be confirmed by optical measurements, such as spectrophotometric reflectance curves which can be determined by measurements on dispersions of the colours over non-reflecting backgrounds.

Such measurements give reflectance curves which conform to the observed colour. Where the coating is of a colourless oxide, there is a progressive shift to longer wave lengths for the reflectance minima as the thickness of the coating increases. For instance, in a series of samples with increasing amounts of TiO_2 in a single coating, the wave lengths of the minimum and maximum reflectance values for typical samples vary with the colour as follows:—

Wave Length of 1st Interference Band.

Colour				Minimum		Maximum	
Silver	...	...	...	In the Ultraviolet		390	millimicrons
Gold	...	...	...	390	millimicrons	700	"
Red	...	...	...	500	"	970	"
Violet	...	...	...	570	"	1100	"
Blue	...	...	...	600	"	1170	"
Green	...	...	...	685	"	1350	"

2nd Interference Band.

Gold (2nd order)	...	430	millimicrons	550	millimicrons
Violet (2nd order)	...	500	"	650	"

When a multilayer coating contains an oxide which is inherently coloured, the spectrophotometric curve shows both the absorption bands of the inherent colour and the interference bands due to the thin film on the translucent flake pigments.

EXAMPLE I.

580 parts of an aqueous titanyl sulphate solution containing 4.4% TiO_2 as titanyl sulphate (equiv. to 25 parts TiO_2) and F.A. of 217 is diluted with 500 parts of water. 100 parts of mica is then suspended in this solution. The mica is a water-ground white mica (muscovite) having the trade name "Concord" (Registered Trade Mark) Wet Ground Mica #200/325. This mica has a specific surface area of about 3.3 square meters per gram, as determined by krypton adsorption in previously mentioned B.E.T. Method; it all passes through a 200 mesh screen and 94% through a 325 mesh screen. The average particle size is in the range of 20—40 microns in maximum dimension and 0.1 micron in thickness. The suspension of mica in the titanyl sulphate solution is heated rapidly for about 10 minutes to the boil and maintained at the boil under reflux for about 2½ hours. The product is isolated by filtering and washing with water to a pH of 5.0. After drying at 80° C., there is obtained about 135 parts of a finely divided flake pigment which requires no further particle size reduction. In bulk form, this flake pigment is a shiny, slightly yellow powder. It may be readily dispersed in various coating composition vehicles by simple high-speed stirring. When dispersed in an alkyd resin vehicle as in Formulation C and coated over a black, primed metal surface, the resulting surface has a silvery appearance and a lustrous iridescent sparkle in sunshine.

EXAMPLE Ia.

This portion of the example illustrates how a change in colour can be obtained by using a larger amount of titanyl sulphate solution, thus depositing a thicker layer of hydrous TiO_2.

If the procedure of Example I is followed except that the amount of titanyl sulphate solution is increased to 1160 parts (50 parts TiO_2), the yield of flake pigment is about 150 parts of shiny powder with a slightly more yellowish tinge. When dispersed in the alkyd resin vehicle and coated over a black primer, a golden appearance and a pleasing lustrous iridescent sparkle are obtained, especially when viewed in sunshine.

EXAMPLE II.

The mica used in this example is of a larger particle size than that used in Example I. It was obtained by screening the mica of the previous example and collecting the portion which passes through a 200 mesh screen and is retained on a 325 mesh screen.

100 parts of this −200/+325 mesh mica

is slurried in 1160 parts of the titanyl sulphate solution of Example I, and the mixture is treated as described in that example. Because of the larger particle size of the mica, the surface area per gram is less, so that the same amount of titanyl sulphate produces a thicker coating on the mica flakes than was obtained in Example Ia. When the flakes are dispersed in a coating composition vehicle and coated over a black surface, a blue appearance and a pleasing lustrous sparkle are obtained.

By using the above conditions and a still larger mica flake which passes a 160 mesh screen but is retained on a 200 mesh screen, the lower surface area results in a still thicker coating of hydrous titanium dioxide. When such flakes are incorporated in a coating composition vehicle and coated over a black surface, a golden appearance and a pleasing lustrous sparkle are seen. The golden appearance obtained with this thicker layer of hydrous titanium dioxide is a second order interference colour.

EXAMPLE III.

The precipitation procedure—used in Examples I and II, and again in this example, coats the mica flake with a translucent layer of hydrous titanium oxide. This example illustrates further the variation in colour with variation in TiO_2 content per unit area together with the changes which occur on calcination of the pigment to convert the hydrous oxide coating to a more light-stable translucent coating of titanium dioxide.

A number of runs were made using the quantities of titanyl sulphate solution and mica set forth in the table below. The mica and titanyl sulphate solution used were the same as those described in Example I. All quantities are in parts by weight. The mica is dispersed in the titanyl sulphate solution, and the resulting mixture is heated to the boil and boiled under reflux for 3 hours, after which time the product is isolated by filtering, washing, and drying in the manner of Example I. The dry product is then calcined in air at about 950° C. for 1 hour. Upon cooling, shiny flakes with an iridescent sparkle are obtained. In bulk form, both the calcined and uncalcined products may be described as being off-white in appearance. However, when dispersed in a liquid and observed on a dark surface, the colours given in the table are observed. These colours vary with the amount of TiO_2 coating on the mica flakes:—

Mica	100	100	100	100
Titanyl Sulphate Solution	772	1160	1600	2440
Equivalent TiO_2	33	50	70	105
Yield—Uncalcined	135	155	178	210
Hydrated TiO_2/Square Meter in grams	0.11	0.17	0.24	0.34
Colour	Pale Gold	Dark Gold	Bluish Violet	2nd Order Pale Gold
Yield after Calcination	123	140	156	182
TiO_2/Square Meter in grams ...	0.085	0.14	0.19	0.27
Colour	Very Pale Gold	Med. Gold	Golden Red	Green

From the above table, it can be seen that there is a loss in the weight of the TiO_2 coating on calcination. Such a loss is, of course, accompanied by some reduction in thickness of the film of TiO_2 and a change in the predominant hue of the interference colours. This change is in the direction of interference at a lower wave length, as is to be expected from thinner films. The calcined products of this example are much more light stable than the uncalcined products of Examples I and II.

EXAMPLE IV.

This example illustrates coating mica flakes using a concentrated titanyl sulphate solution of the type commonly produced during the conversion of ilmenite ore to TiO_2 pigment. Although such solutions usually contain some iron in divalent form, it is not precipitated along with the hydrous TiO_2. Instead, the iron remains dissolved as $FeSO_4$ in the mother liquor. As set forth in detail in the table which follows, 100 parts of mica as described in Example I is slurried in the indicated amount of water and heated to about 60° C. While stirring vigorously at 60° C., the indicated amount of concentrated titanyl sulphate solution ($TiOSO_4$, calculated as TiO_2, 14.1%; $FeSO_4$, calculated as Fe, 3.7%; FA—80) also heated to 60° C., is added rapidly. The mixture is heated to the boil and boiling continued under reflux for the indicated time. The flakes are recovered by filtering, washing free of soluble salts and drying at 80° C. The slightly yellow nacreous flakes are then calcined in air at 950° C. for 1 hour to give slightly darker coloured flakes which, when dispersed in coating compositions, impart the indicated colours to the compositions together with a lustrous iridescent sparkle in the sunshine.

	A	B
Mica	100	100
Water	236	448
Titanyl Sulphate Solution ...	190	365
Equivalent TiO_2	27.3	52.3
Reflux Time ...	2 hours	2.5 hours
Yield	130	165
% hydrous TiO_2	23.1	39.4
Yield after Calcination	127	148
% TiO_2	21.4	35.4
Colour	Silver	Cold

EXAMPLE V.

The interference colour of a coated flake pigment is a function of the thickness of the coating layer thereon. Since actual measurement of this thickness is not readily done, the weight of the coating material per unit area of the surface of the substrate is a convenient index of the thickness of the coating. It is obvious that a fixed weight of coating material will produce coating of different thickness on equal weights of substrates which differ in surface area. Conversely, adjustment of the weight of substrates so that the total surface areas are equal should give equal coating and substantially equal colour. The following series of samples illustrates these points using three samples of water-ground white mica (muscovite) with the weights adjusted so that the total surface areas of the mica used is the same in each case.

The titanyl sulphate solution had the following composition: $TiOSO_4$, calculated as TiO_2, 14.1%; $FeSO_4$, calculated as Fe, 3.7%; FA—80. The general procedure used to coat the mica is described in Example IV. Specific details on the procedure are as follows:—

Surface Area and Weight of Samples:

	Sample 1	Sample 2	Sample 3
Surface area of mica, sq. meters/g. ...	3.2	2.6	2.4
Weight of mica used in grams	20.0	24.6	26.7
Total surface area of mica, sq. meters ...	64.0	64.0	64.0

Treatment as follows:

	Sample 1	Sample 2	Sample 3
a. Weight of $TiOSO_4$ (calc. as TiO_2)—grams	11.7	11.7	11.7
Yield in grams	29.9	34.2	36.4
Weight of hydrated TiO_2 in coated flakes	9.9	9.6	9.7
Hydrated TiO_2/sq. meter of Mica in gr.	0.16	0.15	0.15
Interference Colour—all three alike ...		light gold	
b. Weight of $TiOSO_4$ (calc. as TiO_2)—grams	15.6	15.6	15.6
Yield in grams	33.1	37.0	39.9
Weight of hydrated TiO_2 in coated flakes	13.1	12.4	13.2
Hydrated TiO_2/sq. meter of mica in gr.	0.20	0.19	0.21
Interference Colour—all three alike ...		reddish gold	
c. Weight of $TiOSO_4$ (calc. as TiO_2) gr.	19.5	20.8	20.8
Yield—grams	36.5	41.5	43.6
Weight of hydrated TiO_2 in coated flakes	16.5	16.9	16.9
Hydrated TiO_2/sq. meter of mica in gr.	0.26	0.26	0.26
Interference Colour—all three alike ...		blue	

EXAMPLE VI.

In a specific examination of the particle size of the TiO_2 deposited on the mica flakes, a sample of uncalcined silver coloured flake pigment may be prepared according to the following procedure which differs only in minor details from Sample A in Example IV above.

100 parts of water-ground white mica (specific surface 3.2 sq. meters/gram) is slurried in 1000 parts of water and the slurry heated externally to about 95° C. At this point, 290 parts of a titanyl sulphate concentrate (15% available TiO_2— F.A. 80) is added rapidly to the agitated slurry. The resulting slurry (Temp. 89° C.) is heated to the boil and boiled for 1.5 hours, cooled to 60° C., filtered, washed free of sulphate ion and dried to give 135 parts of a yellowish silver nacreous pigment. Portions of this pigment are then calcined in air at various temperatures as shown in the table below. The final flakes, after calcination, are then examined in a conventional manner in an electron microscope and the general appearance of the samples, together with an estimate of average particle size, is presented in the table. Three other samples prepared in a like manner and similarly examined in the electron microscope are included in the table.

Sample	Calcination Temp.	General Appearance	Particle Size (Microns)
This Example	Uncalcined	Indefinite particles—very small	Not measurable
" "	700° C.	Uniform discrete particles	0.025
" "	900° C.	" " "	0.04
" "	1000° C.	" " "	0.09
" "	1100° C.*	Many lath-like particles of non-uniform sizes	>0.10
Sample A	950° C.	Discrete particles	0.08
Sample B	900° C.	Discrete particles	0.03
" "	950° C.	" "	0.07
Sample C	850° C.	Discrete particles	0.04
" "	950° C.	" "	0.07

*It should be noted that at temperatures of 1100° C. and above the mica begins to decompose and the crystal growth of TiO_2 becomes much more rapid.

EXAMPLE VII.

This example illustrates the use of an organic titanate to apply a titanium oxide layer to the mica flakes.

Approximately 1 gram of muscovite mica flakes with largest dimensions of about 100 microns and with a thickness of 1—2 microns is spread in a thin layer inside a 1-inch "Vycor" (Registered Trade Mark) tube. The tube is evacuated by means of a vacuum pump attached to one end of the tube, the other end of the tube being attached through a closed valve to a reservoir of tetraisopropyl titanate contained in a glass flask. The tube and flask contents are heated, with maintenance of the vacuum, to 600° C., at which temperature the valve between the tube and the organic titanate container is opened permitting the titanate vapors to pass into the hot tube. After approximately 30 minutes, the valve is closed and the tube and contents are cooled to room temperature under vacuum. After cooling, the vacuum is disconnected and the coated flakes are removed from the tube. The flakes obtained exhibit a variety of interference colours and when they are dispersed in a cellulose acetate film, they impart a nacreous appearance thereto.

EXAMPLE VIII.

This example illustrates improving the light stability of the hydrous titanium dioxide coating by applying an outer coating of hydrous aluminum oxide on the TiO_2-coated mica flakes.

100 parts of the yellowish-white flake of Example Ia is neutralized by slurrying in an excess of dilute aqueous ammonia. It is then filtered, washed, dried, if desired, and reslurried in 4000 parts of an aqueous solution containing 200 parts of $Al_2(SO_4)_3$. $18H_2O$ and 80 parts of sodium acetate.

The slurry is heated to 90° C. and then held in the temperature range of 90° C.—100° C. for about 30 minutes. The slurry is filtered hot, washed with hot water until free of sulphates, and dried at about 60° C. to give a powder containing about 6% alumina (as Al_2O_3). This powder is more yellowish than the starting material, and when it is dispersed in an alkyd coating composition, such as Formulation D, and applied over a black primer, a dark golden nacreous appearance and a lustrous iridescent sparkle are obtained. When tested in a "Fade-Ometer" (Registered Trade Mark), a cellulose acetate film (as in Formulation A) pigmented with these flakes shows a marked superiority in light stability over the untreated counterpart.

EXAMPLE IX.

This example illustrates a still further improvement in light stability by applying a layer of hydrous aluminum oxide to a calcined TiO_2-coated mica flake pigment.

100 parts of the calcined product of Example III resulting from the use of 100 parts of mica and 772 parts of titanyl sulphate solution is mixed with 200 parts of an aqueous solution containing 20 parts of $Al_2(SO_4)_3$.$18H_2O$. A 5% solution of sodium carbonate is then added slowly, while stirring, until the pH is 7.0 The flake pigment is then isolated by filtering, washed free of soluble salts, and dried. The product obtained is substantially unchanged with respect to sparkle and overall silvery gold appearance when dispersed in a coating composition vehicle and applied over a black surface. On the other hand, it exhibits a notable improvement in lightfastness. Cellulose acetate films containing the pigment show no change upon exposure in an Atlas "Fade-Ometer" (Registered Trade Mark) for 1000 hours.

EXAMPLE X.

This example illustrates the use of synthetic phlogopite as the micaceous flake substrate.

20 parts of synthetic phlogopite of such particle size that all of it passes through a 160 mesh screen and is retained by a 200 mesh screen, is added at room temperature (approximately 25° C.) to 600 parts of aqueous titanyl sulphate solution containing 24 parts of titanyl sulphate calculated as TiO_2 and F.A. of 217. The mixture is stirred and diluted with 600 parts of water and then heated to 80° C. during one hour and maintained at 70—80° C. with vigorous stirring. Portions of the slurry are removed from time to time and placed in a pool of water on a back surface for determination of colour. After 1½ hours at 70—80° C. a blue colour is evident. On continued stirring to a total of 3 hours, the colour of samples taken during the stirring period becomes successively gold, red, blue, green, gold (again), red (again), and then, finally, green. The slurry is then filtered, and the filter cake is washed with water until the effluent wash water gives a negative test for sulphate ion. The filter cake is then washed with acetone and allowed to dry. The final product is a flake pigment having a predominant green hue and a lustrous iridescent sparkle when dispersed in an alkyd resin and viewed in sunshine.

EXAMPLE XI.

This example illustrates the application of a hydrous zirconium oxide to mica flakes.

100 parts of the mica described in Example 1 is slurried in 2000 parts of an aqueous solution containing 200 parts of $Zr(SO_4)_2.4H_2O$ and previously adjusted to a pH of 2.8 by adding urea thereto. The slurry is heated to 90° C. and held near this temperature for about 2 hours with good agitation throughout. The solid product is recovered by filtering, washed, dried, and is then calcined for 1 hour at 700° C. in air to give a flake pigment having a silver appearance and a pleasing lustrous sparkle when dispersed in a coating composition vehicle.

EXAMPLE XII.

This example illustrates the application of a layer of hydrous zinc oxide to mica flakes which have been previously coated with TiO_2.

The procedure of Example Ia is followed to produce TiO_2-coated mica flakes and, prior to drying, 30 parts of these flakes is slurried in 2200 parts of 3% aqueous ammonium hydroxide solution at room temperature. The mixture is stirred at room temperature for 30 minutes, and then filtered. The presscake is washed with water until the pH of the effluent wash water is 8, and then dried in an oven at 80° C. 25 parts of the dried flakes is added at room temperature to a solution formed as follows: 10 parts of $ZnCl_2$ is dissolved in 500 parts of water, and ammonium hydroxide is then added to the solution with vigorous stirring until the precipitate initially formed redissolves. The slurry is heated to 80° C. and maintained at that temperature for about 2 hours to drive off ammonia from the solution. After the heating, the slurry is filtered and the presscake is washed free of soluble chlorides and dried at 80° C. The product obtained has much the same appearance as the product of Example Ia. Analysis indicated the presence of 19% zinc, calculated as zinc oxide. Lightfastness of the zinc-treated product is appreciably superior to that of the corresponding product without the zinc treatment. Calcination of this zinc-containing product yields a flake pigment in which the TiO_2 is present predominantly in the rutile form, whereas in the corresponding calcined flake product which is not zinc-treated, the TiO_2 is predominantly in the anatase structure.

EXAMPLE XIII.

This example illustrates the application of a layer of hydrous zirconium oxide to mica flakes which have been previously coated with TiO_2.

A TiO_2-coated mica flake pigment exhibiting a golden colour when observed on a black surface is prepared as follows: 108 parts of water-ground muscovite mica with a surface area of 3.1 square meters per gram is slurried in 600 parts of water. The slurry is heated to the boil, and 351 parts of a 20% (as TiO_2) titanyl sulphate solution (F A. 80) is added to the boiling slurry. Heating is continued, and the mixture is refluxed for 3 hours and allowed to cool overnight before filtering. After filtering, the presscake is washed with 12,000 parts of water at room temperature, then washed with 500 parts of a 2% ammonium hydroxide solution, and finally washed with 6000 parts of water. After drying the presscake for 12 hours at 80° C., 164 parts of flake pigment is obtained, containing about 34% of hydrous titanium oxide. When dispersed in a coating composition vehicle, these flakes exhibit a reddish gold colour which is more pronounced over a dark surface.

50 parts of these golden flakes is then overcoated with hydrous zirconium oxide as follows: 7.5 parts of $Zr(SO_4)_2.4H_2O$ is dissolved in 500 parts of water, and urea is then added slowly to the solution with

good stirring to bring the pH to 2.0. 50 parts of the golden flakes is added to the solution, the resulting slurry is heated to the boil and held at the boil under reflux for 1 hour. On heating, the initial golden colour of the flakes gradually changes to a purple. Addition of more of the zirconium sulphate-urea solution and further heating results in a second order gold colour to the flakes. The slurry is then filtered, and the solid is washed free of sulphate and dried to give a pigment which exhibits a golden colour when dispersed in a coating composition vehicle and applied over a black surface. Accelerated light-fastness tests show the zirconium-coated flakes to be appreciably better in lightfastness than the uncoated counterpart. They contain 7.7% zirconium oxide (as ZrO_2).

The following Examples XIV to XVIII, inclusive, are based upon the use of TiO_2-coated mica flakes, made after the general procedure of Example IV, which are further coated with a second metal oxide as shown in the details. In these examples, two different samples are shown:—one of these samples (Flake A) is an uncalcined silver-coloured flake containing 20.7% TiO_2. This product was prepared by treating 100 parts of the mica described in Example I with 233 parts of a titanyl sulphate concentrate containing 15% TiO_2 (F A. 80) (which is equal to 35 parts TiO_2). The procedure used is according to Example IV and 126 parts of flake are obtained. Prior to drying the residual sulphate acid is neutralized by slurrying in an excess of dilute ammonia, filtering, and washing. The second sample (Flake B) is a yellowish silver-coloured flake containing 26.2% TiO_2 made in a like manner from 100 parts mica described in Example I and 290 parts titanyl sulphate concentrate (F A. 80) containing 15% TiO_2, which is equal to 43.5 parts TiO_2.

In Example XIV to XVIII inclusive, the term "reflex colour" is used to describe the colour observed at the specular angle, usually contrasting with the inherent colour. In this use, it is a convenient means of distinguishing the interference colour from the inherent colour of metal oxide coatings.

EXAMPLE XIV.

This example and Example XIVa illustrate the application of a layer of chromium oxide to mica flakes which have been previously coated with TiO_2.

$Cr(NH_3)_6Cl_3$ is prepared by dissolving 40 parts of $CrCl_3$ in liquid ammonia and allowing the excess ammonia to evaporate. The light green product thus obtained is dissolved in 2000 parts of water and then 100 parts of TiO_2-coated mica (Flake A) is added with stirring. The slurry is heated to the boil and refluxed for about 4 hours until the green colour of the solution is no longer evident. The product is then isolated by filtering, washed with water, and dried. The flake pigment product is light green in colour, and at the same time this green colour exhibits a silvery reflex.

On calcination at 950° C., the green colour becomes somewhat less intense, but the silver reflex is retained. This product, containing chromium oxide equivalent to 3.04% Cr, is markedly more lightfast than the untreated Flake A.

EXAMPLE XIVa.

100 parts of yellowish silver Flake B (26.2% TiO_2) is slurried in a solution of 40 parts chromium sulphate ($Cr_2(SO_4)_3.5H_2O$) in 100 parts of water at 50° C. Borax ($Na_2B_4O_7.10H_2O$) is then added in small increments of 2 parts each until a constant pH of 5.5 to 6.0 is reached and maintained for at least 15 minutes. The resulting product is isolated by filtering, washed sulphate free, and dried. After calcination for ½ hour at 900° C., the flakes are greenish gold in colour with a golden reflex, and they exhibit excellent lightfastness in the cellulose acetate film of Formulation A.

EXAMPLE XV.

This example and Example XVa illustrate the application of a layer of iron oxide to mica flakes which have been previously coated with TiO_2.

400 parts of silver-coloured Flake A (20.7% TiO_2) is added to a solution of 50 parts ferric chloride ($FeCl_3$) and 80 parts of sodium acetate ($NaC_2H_3O_2$) in 100 parts of water at 25° C. The slurry is heated with agitation to 80° C. and stirred for one hour at 80° C. until the mother liquor is substantially colourless. A further portion of solution containing 50 parts ferric chloride and 80 parts sodium acetate in 1000 parts of water is then added. The mixture is heated for one hour at 80° C., after which time another 50 parts of ferric chloride and 80 parts of sodium acetate in 1000 parts of water is added, and the whole mixture is heated for one hour at 80° C. The slurry is filtered, washed, and dried to give yellowish-brown flakes having a golden reflex. Upon calcination at 400° C., 600° C., and 900° C., the pigment being maintained at each temperature for ½ hour, the golden reflex does not change but the overall colour changes to brown at 400° C., to reddish brown at 600° C., and to a brilliant golden brown at 950° C.

EXAMPLE XVa

100 parts of the yellowish silver Flake

B (26.2% TiO_2) is added to 600 parts of a 11.4% $FeCl_3$ solution (68 parts $FeCl_3$) and 60 parts of sodium acetate ($NaC_2H_3O_2$) is added with agitation. After the sodium acetate is dissolved, the slurry is heated to 80° C. and maintained at that temperature for several hours with frequent examination of a diluted drop of the slurry on a black surface. The overall colour of the flakes is golden yellow, and the coloured sparkle or reflex colour progresses with continued heating through gold to red, to purple, and finally to green, while the overall golden colour remains substantially unchanged. Samples are taken when each of the various colours is observed, and these samples are filtered, washed, and dried, and analyzed for iron. This analysis indicates the following iron content: —

	% Fe
Red reflex colour	8.9
Purple reflex colour	11.0
Green reflex colour	16.4

These samples, in addition to possessing the unusual colour effects described above, show marked improvements in lightfastness as compared with the original TiO_2-coated flakes.

EXAMPLE XVI.

This example and Example XVIa illustrates the application of a layer of nickel oxide to mica flakes which have been previously coated with TiO_2.

100 parts of silver-coloured Flake A is added to a solution prepared by dissolving 200 parts of nickel chloride ($NiCl_2.6H_2O$) and 500 parts of sodium acetate ($NaC_2H_3O_2$) in 2400 parts of water. The resulting slurry is heated to the boil and kept at the boil for about 4 hours until the flakes become light green in colour. The product is then filtered, washed chloride free, and dried at 60° C. The dried material is a light green colour with a sparkling silver appearance. A portion of the dried flakes is calcined by heating to 950° C. and maintaining the flakes at this temperature for 30 minutes. The calcined product has a bright yellow colour with a sparkling golden reflex. It contains 3.5% Ni. When dispersed in a vinyl composition (as in Formulation D) a particularly pleasing golden nacreous effect is obtained.

EXAMPLE XVIa.

An ammonical nickel chloride solution is prepared by dissolving 24 parts nickel chloride ($NiCl_2.6H_2O$) in 2000 parts of water and adding concentrated ammonium hydroxide solution with constant stirring until a precipitate is formed and then re-

dissolved. 100 parts of silver-coloured Flake A (20.7% TiO_2) is added, the slurry heated to the boil and maintained at the boil under reflux for about 4 hours. It is then filtered, washed free of chlorides, and dried to give light green coloured flakes with a silver reflex, showing a marked improvement in light stability over the untreated silver flakes.

EXAMPLE XVII.

This example illustrates the application of a layer of cobalt oxide to mica flakes which have been previously coated with TiO_2.

100 parts of silver-coloured Flake A is added with stirring to a solution at room temperature prepared by dissolving 200 parts of cobalt chloride hexahydrate ($CoCl_2.6H_2O$) and 300 parts of sodium acetate in 200 parts of water. The resulting slurry is heated to the boil and kept under reflux for one hour. The slurry is then filtered hot and the presscake is washed with water until chloride free. The presscake is dried in an oven at 80° C. The dried flakes, when dispersed in cellulose acetate as described in Formulation A produce a dry film having a gray metallic nacreous appearance. Calcination of the flakes for one hour at 950° C. results in a light green product having a silver reflex colour. The product contains 2.9% Co.

EXAMPLE XVIII.

This example illustrates the application of a layer of copper oxide to mica flakes which have been previously coated with TiO_2.

100 parts of silver-coloured Flake A is added to an ammoniacal copper chloride solution prepared by dissolving 20 parts of copper chloride ($CuCl_2$) in 1000 parts of water and then adding ammonium hydroxide (28% NH_3) until a precipitate is formed and then redissolved. The slurry is gently heated at about 60° C. for one hour to drive off ammonia and precipitate a hydrous copper oxide on the mica. The flake product is then isolated by filtering, washed free of dissolved salts, and dried. The product consists of grayish flakes with a silver reflex. Calcination of a portion of the product at 950° C. for 15 minutes gives a darker gray-black product retaining the silver reflex and containing 2.4% Cu.

EXAMPLE XIX.

Coprecipitation with Chromium Oxide.

40 parts of chromic sulphate ($Cr_2(SO_4)_3$. $5H_2O$) is dissolved in 100 parts of water to which is added 100 parts of water-ground white mica (Concord #200/325) and the slurry is heated, while well stirred, to 90—100° C. 490 parts of titanyl sul-

phate concentrate (TiO$_2$ equivalent 14.4%
—F A. 80) is then added rapidly, the slurry
is reheated rapidly to the boil and main-
tained under reflux for about 3 hours. The
product is filtered, washed free of soluble
salts and dried to give greenish flakes with
a reddish gold reflex colour. On calcina-
tion at 900° C., the product is transformed
to yellow nacreous flakes with a brilliant
gold reflex colour. Coating compositions
containing this pigment exhibit excellent
lightfastness.

EXAMPLE XX.
Coprecipitation with Iron Oxide.

100 parts of Concord Water Ground
Mica #200/325 is slurried in 920 parts of
a titanyl sulphate solution (TiO$_2$ equivalent
4.15% F A. 220) into which is dissolved 20
parts of anhydrous ferric sulphate. The
slurry is thoroughly agitated and heated to
95—100° C. in about 30 minutes and held
at that temperature for about 4 hours.
Samples of the slurry taken during the
heating period and diluted with water on
a black surface show a progressive change
in the colour of the mica flakes suspended
therein. The final pigment is filterered,
washed free of soluble salts and calcined
for one hour at 900° C. to give a yellow
nacreous flake pigment which produces a
strongly golden colour in a coating com-
position. Such compositions exhibit a
very high degree of lightfastness.

EXAMPLES XXI and XXII.
The following examples illustrate the use
of mixtures of the new nacreous flake pig-
ments with conventional coloured pigments
to obtain highly attractive decorative
effects.

*Example XXI—Acrylic lacquers with mix-
tures of pigments.*
These lacquers are based upon a Vehicle
Blend consisting of:—

85.4% mixed acrylic ester Polymer
       (Acryloid A-101)
14.6% butyl benzyl phthalate (as plas-
       ticizer)
and a Solvent Blend consisting of:—
20% monoacetate of ethylene glycol
     monoethyl ether
30% methyl ethyl ketone
50% Toluene

A copper phthalocyanine (CPC) blue
acrylic lacquer (made in a conventional
manner in a ball mill) consists of:—

3.2 parts Copper Phthalocyanine Blue
66.2 parts Vehicle Blend
30.6 parts Solvent Blend

The following mixed lacquers are then
made.

	A		B	
Silver Flake Pigment (Example V*a*)	4.75	parts	4.75	parts
Vehicle Blend	97.0	„	97.0	„
CPC Blue Lacquer	7.8	„	1.6	„
Solvent Blend	21.7	„	21.7	„

The ingredients are thoroughly blended
by high speed agitation for 15 minutes,
thinned with additional solvent blend to
spraying consistency and sprayed with 3
double coats on a suitable panel.
In lacquer A, the silver flake/blue ratio
is 95/5 and the resulting panel exhibits a
highly pleasing "metallized" effect with a
more pronounced sprakle than usually ex-
hibited by lacquers containing aluminum
flake. The effect is obtained over a fairly
wide range or flake/colour ratios up to
as much as 50/50.
In lacquer B, the silver flake/blue ratio is
99/1 and the resulting panel exhibits the
effect of a bluish toned pearl with a
brilliant iridescent sparkle under bright
illumination.

*Example XXII—Alkyd enamel with a mix-
ture of pigments.*
A polychloro copper phthalocyanine
green (CPC green) enamel of the following
composition is prepared by dispersion in a
ball mill in the conventional manner:—

5.0 parts CPC Green pigment
42.6 parts non-oxidizing coconut oil—
       modified alkyd resin solution (60%
       solids)
20.0 parts modified melamine formalde-
       hyde resin (55% solids)
16.2 parts aromatic hydrocarbon solvent
16.2 parts aliphatic hydrocarbon solvent

A portion of this enamel is mixed with
a nacreous flake pigment as follows:—

	Parts
Gold flake pigment (Example V*b*)	4.75
CPC Green enamel	5.00
Non-oxidizing coconut oil— modified alkyd resin solution (60% solids)	58.4

These ingredients are mixed for

minutes by high speed agitation after which 27.2 parts of modified melamine formaldehyde resin (55% solids) is added and high speed agitation is continued for 5 minutes. The enamel is then reduced to spraying consistency with a 50/50 aromatic/aliphatic hydrocarbon mix and sprayed with 3 double coats onto a suitable panel. This enamel contains a gold flake/CPC Green ratio of 95/5 and the colour is much yellower than that of the CPC Green enamel alone. In addition, the panels exhibit a lustrous golden sparkle.

EXAMPLE XXIII.

200 parts of $FeCl_3$ (anhydrous) is dissolved in 2000 parts of water at room temperature to which is added 40 parts of sodium acetate ($NaC_2H_3O_2$) and 100 parts of wet ground muscovite mica sold under the name "Concord" (Registered Trade Mark) Wet Ground Mica #200/325 which all passes through a 200 mesh screen and 90% through a 325 mesh screen, has an average diameter of flake particles in the range 10 microns to 50 microns, and a surface area of 3.2 square meters per gram. The mixture is heated rapidly to 70° C. while well stirred and held at 70° C. for one hour. After heating for a few minutes, the mica flakes in the slurry take on the golden-yellow appearance of hydrous ferric oxide. When a sample of the slurry is diluted and observed against a black background, in addition to the overall golden yellow appearance, a brilliant coloured sparkle appears as a reflex colour from a bluish silver with a short heating period to a true silver at the end of heating. This reflex colour is an interference colour resulting from the deposition of the metal oxide film on the surface of the mica, the thickness of the film and, hence, the colour, varying with increasing time of heating. At the end of the heating period, the product is filtered, washed free of chloride ions and dried. It contains 18.1% iron (as Fe_2O_3) and is a golden yellow powder which shows a brilliant sparkle when rubbed out to a thin film. When dispersed in a typical coating composition, as the alkyd enamel of Formulation C, and applied to a metal panel, the resulting light stable finish is golden yellow with a predominately silver reflex. When viewed under bright illumination, at the specular angle, a brilliant play of iridescent colours is also seen. When dispersed in an unsupported vinyl film (as in Formulation D) a brilliant golden, nacreous plastic composition is obtained.

It is apparent that the amount of iron oxide deposited influences the interference colour and may be varied by variations in the time of heating or by variations in the amount used.

EXAMPLE XXIV.

The iron oxide-coated flakes of Example XXIII are calcined by heating in the air at temperatures within the range 400—700° C., the resulting overall colour ranging from a brown at 400° C. to a purple at 600—700° C. and a silver reflex colour at all temperatures. As calcination processds to higher temperatures, the interference colour is lessened and largely disappears at temperatures above 700° C. The product becomes a red pigment without nacreous character at 950° C. Examination under a microscope of the uncalcined flakes and those calcined in the lower temperature ranges reveals a uniform layer of metal oxide particles which are extremely small and indistinct in the uncalcined product. As the temperature is increased, the particles developed a distinct character, but remain below 0.1 micron in size until the temperature exceeds about 700° C.

EXAMPLE XXV.

40 parts of chromic sulphate ($Cr_2(SO_4)_3$. $5H_2O$) is dissolved in 200 parts of water at room temperature and 100 parts of water ground white mica (average size 10—50 microns) is added. Powdered borax ($Na_2B_4O_7.10H_2O$) is slowly added to the agitated slurry so that the pH of the slurry is maintained at about 5.0 to 5.5. Under these conditions, a hydrous chromium oxide is precipitated slowly and deposits preferentially on the surface of the mica flakes as a uniform thin film which results in an interference colour that changes from gold to red to blue as the amount of hydrous chromic oxide precipitated increases. The addition of small portions of borax is continued until all of the chromic sulphate has been precipitated and the product is then filtered, washed free from sulphate ions and dried to give a light green powder (12% chromium as Cr_2O_3) with a blue reflex colour when spread in a thin film as when rubbed between the fingers. When used to pigment a cellulose acetate film, as in Formulation A, the lightfast film has a light green colour with a pronounced blue reflex. Examination of these flakes under the electron microscope shows the flakes to be uniformly covered with the hydrous oxide film.

Calcination of these coated flakes in air at 700° C. for ½ hour gives a green product of somewhat less intensity but with a silver-blue interference colour. The particles of chromic oxide on the mica are less than 0.1 micron in diameter.

EXAMPLE XXVI.

40 parts of vanadyl sulphate ($VOSO_4$.

2H$_2$O) is dissolved in 1600 parts of water at room temperature and 100 parts of wet ground white mica ("Concord" (Registered Trade Mark) Wet Ground Mica #200/325) is added to the solution. While keeping the slurry well stirred, powdered borax (Na$_2$B$_4$O$_7$.10H$_2$O) is added in small increments at a rate sufficient to maintain the pH in the range 3.5—4.5 whereupon vanadium tetroxide is deposited on the mica flakes to give a brownish gray colour in overall appearance together with an interference colour which varies from silver to gold to red as the quantity of coating increases. The product is filtered, washed free of sulphate ions and dried to give brownish gray flakes. When these flakes are calcined in air at 300—400° C., they are transformed to light yellow flakes with an intense silver-blue reflex colour. These yellow flakes have a coating of about 15% vanadium pentoxide (V$_2$O$_5$) resulting from the simultaneous calcination and oxidation of the hydrous tetroxide. The particles of vanadium pentoxide are less than about 0.1 micron in diameter. If the calcination temperature is increased substantially beyond 400° C., there is pronounced tendency for particle growth and loss of nacreous character.

Articles pigmented with these yellow flakes exhibit a brilliant yellow colour with a silver-blue reflex. They are light stable products.

EXAMPLES XXVII and XXVIII.

The following examples illustrate the use of mixtures of the new nacreous flake pigments with conventional coloured pigments to obtain highly attractive decorative effects.

Example XXVII—Acrylic lacquers with mixtures of pigments.

These lacquers are based upon a Vehicle Blend consisting of:—

85.4% mixed acrylic ester Polymer (Acryloid A-101)
14.6% butyl benzyl phthalate as (plasticizer)

and a Solvent Blend consisting of:—

20% monoacetate of ethylene glycol monoethyl ether
30% methyl ethyl ketone
50% toluene

A copper phthalocyanine (CPC) blue acrylic lacquer (made in a conventional manner in a ball mill) consists of:—

3.2 parts Copper Phthalocyanine Blue
66.2 parts Vehicle Blend
30.6 parts Solvent Blend

The following mixed lacquers then made:—

	A	B
Golden Flake Pigment (Exam. I)	4.75 parts	4.75 parts
Vehicle Blend	97.0 „	97.0 „
CPC Blue Lacquer	7.8 „	1.6 „
Solvent Blend	21.7 „	21.7 „

The ingredients are thoroughly blended by high speed agitation for 15 minutes, thinned with additional Solvent Blend to spraying consistency and sprayed with 3 double coats on a suitable panel.

In lacquer A, the golden flake/blue ratio is 95/5 and the resulting panel exhibits a highly pleasing "metallized" effect of a greenish hue and with a more pronounced sparkle than usually exhibited by lacquers containing aluminum flake. The effect is obtained over a fairly wide range of flake/colour ratios up to as much as 50/50.

In lacquer B, the golden flake/blue ratio is 99/1 and the resulting panel exhibits a bluish green toned nacreous effect with a brilliant iridescent sparkle under bright illumination.

Example XXVIII—Alkyd enamel with a mixture of pigments.

A polychloro copper phthalocyanine (CPC green) enamel of the following composition is prepared by dispersion in a ball mill in the conventional manner:—

5.0 parts CPC Green pigment
42.6 parts non-oxidizing coconut oil—modified alkyql resin solution (60% solids)
20.0 parts modified melamine formaldehyde resin (55% solids)
16.2 parts aromatic hydrocarbon solvent
16.2 parts aliphatic hydrocarbon solvent

A portion of this enamel is mixed with a nacreous flake pigment as follows:—

	Parts
Gold flake pigment (Example I)	4.75
CPC Green enamel	5.00
Non-oxidizing coconut oil—modified alkyd resin solution (60% solids)	58.4

These ingredients are mixed for 5 minutes by high speed agitation after which 27.2 parts of modified melamine formaldehyde resin (55% solids) is added and high speed agitation is continued for 5 minutes. The enamel is then reduced to spraying consistency with a 50/50 aromatic/aliphatic hydrocarbon mix and sprayed with 3 double coats onto a suitable panel. This enamel contains a gold flake/CPC Green ratio of 95/5 and the colour is much yellower than that of the CPC Green enamel alone. In addition, the panels exhibit a lustrous golden sparkle.

The pigments described in the foregoing Specification offer the following notable advantages: —

1. They can be prepared and marketed as dry pigments.
2. These dry pigments show a remarkable ease of dispersion in the compositions in which they are used.
3. They show a nacreous effect of a degree not readily produced with prior art nacreous pigments.
4. They show an iridescent sparkle many of them having a pronounced predominant hue which may be carried at will by simple alterations in the compositions.
5. When properly stabilized, they offer a high degree of lightfastness.
6. Most of them are chemically stable and they do not contribute to water spotting of surfaces finished with compositions containing them.
7. They are heat stable and can be used in baking enamels and in plastics processed at high temperature.
8. They are completely non-bleeding in solvents and in the usual chemical agents to which coating compositions may be subjected.
9. They are compatible with coating composition vehicles and plastic systems commonly met.
10. They make possible tinctorial effects not heretofore obtainable.

WHAT WE CLAIM IS:—

1. A pigment composition comprising a translucent micaceous flake substrate carrying on the surface of the flakes a translucent metal oxide layer consisting of particles, substantially all of which are less than 0.1 micron in size, of hydrous titanium dioxide, titanium dioxide, hydrous zirconium dioxide, zirconium dioxide, ferric oxide, chromic oxide, vanadium pentoxide, hydrous ferric oxide, or hydrous chromic oxide, or a mixture of two or more of these.

2. A pigment composition according to Claim 1, wherein the metal oxide layer is 20—250 millimicrons thick.

3. A pigment composition according to any one of the preceding claims, wherein the substrate consists of white mica flakes.

4. A pigment composition according to Claim 3 comprising a silver pigment composed of white mica flakes having on their surface a transducent layer 20—40 millimicrons thick of titanium dioxide particles.

5. A pigment composition according to Claim 3 comprising a gold pigment composed of white mica flakes having on their surface a translucent layer 40—90 millimicrons thick of titanium dioxide particles.

6. A pigment composition according to Claim 3 comprising a red pigment composed of white mica flakes having on their surface a translucent layer 90—110 millimicrons thick of titanium dioxide particles.

7. A pigment composition according to Claim 3 comprising a violet pigment composed of white mica flakes having on their surface a translucent layer 110—120 millimicrons thick of titanium dioxide particles.

8. A pigment composition according to Claim 3 comprising a blue pigment composed of white mica flakes having on their surface a translucent layer 120—135 millimicrons thick of titanium dioxide particles.

9. A pigment composition according to Claim 3 comprising a green pigment composed of white mica flakes having on their surface a translucent layer 135—155 millimicrons thick of titanium dioxide particles.

10. A pigment composition according to any one of Claims 1—3, wherein the translucent metal oxide layer comprises titanium dioxide in an amount of 50—600 milligrams per square metre of surface area of the micaceous flakes.

11. A pigment composition according to any one of Claims 1—3, wherein the metal oxide layer constitutes 10—66% by weight of the pigment and consists of hydrous titanium dioxide particles, titanium dioxide particles, hydrous zirconium dioxide particles or zirconium dioxide particles, or two or more of these.

12. A pigment composition according to any one of Claims 1—3, wherein the metal oxide layer constitutes 10—40% by weight of the pigment and consists of ferric oxide, chromic oxide, vanadium pentoxide, hydrous ferric oxide or hydrous chromic oxide.

13. A pigment composition according to Claim 12, wherein the metal oxide is present in an amount of 50—280 milligrams per square metre of surface area of the micaceous flake.

14. A pigment composition according to Claim 12, wherein the metal oxide layer is 30—200 millimicrons thick.

15. A pigment composition according

to any one of the preceding claims wherein the micaceous flakes have a surface area of 2—7 square metres per gram.

16. A pigment composition according to any one of Claims 1—3, wherein the substrate flakes carry on their surface a first layer of titanium dioxide, hydrous titanium dioxide, zirconium dioxide or hydrous zirconium dioxide, and on top of this first layer at least one layer of a different metal oxide selected from titanium oxide zirconium oxide, alumina, zinc oxide, antimony oxide, tin oxide, iron oxide, copper oxide, nickel oxide, cobalt oxide, chromium oxide, and the hydrated forms of these oxides.

17. A pigment composition according to any one of Claims 1— 3, wherein the metal oxide layer comprises as its major component titanium dioxide, zirconium dioxide, hydrous titanium dioxide or hydrous zirconium dioxide, and also, intermingled therewith a minor proportion of one or more different metal oxides selected from titanium oxide, zirconium oxide, alumina zinc oxide, antimony oxide, tin oxide, iron oxide, copper oxide, nickel oxide, cobalt oxide, chromium oxide, and the hydrated forms of these oxides.

18. A pigment composition according to Claim 1 substantially as hereinbefore described.

19. An article of manufacture having deposited thereon a pigment composition claimed in any one of Claims 1—18.

20. A coating composition comprising a major amount of a film-forming material and a minor amount of a pigment composition claimed in any one of Claims 1—18.

21. An unsupported plastic film comprising a major amount of a film-forming polymer and a minor amount of a pigment composition claimed in any one of Claims 1—18.

22. A process for the production of a pigment composition having a micaceous flake substrate, which comprises suspending the substrate flakes in a dilute acidic solution of a titanium, zirconium, iron, chromium or vanadium salt capable of forming by hydrolysis a hydrous oxide, and bringing about a slow hydrolysis at a rate at which the micaceous flakes function as nuclei for the formation of a hydrous oxide layer on their surfaces.

23. A process according to Claim 22,

wherein the salt is titanyl sulphate, titanium oxychloride, titanium acetyl acetonate, or triethanolamine titanate.

24. A process according to Claim 22, wherein the salt is zirconium oxychloride or zirconium sulphate.

25. A process according to Claim 22, wherein the salt is ferric chloride or sulphate.

26. A process according to Claim 22, wherein the salt is chromic sulphate or chloride.

27. A process according to Claim 22, wherein the salt is vanadyl sulphate.

28. A process according to Claim 23, wherein the acidic solution contains besides a titanium salt, a salt of antimony, cobalt, chromium, tungsten, molybdenum or iron in amount such that the amount of metal oxide deposited therefrom does not exceed 20% of the titanium oxide deposited.

29. A process according to any one of Claims 23—30, wherein the hydrous metal oxide deposited is subsequently calcined, at a temperature less than 1000° C. in the case of titanium dioxide, less than 800° C. for iron oxide, less than 700° C. for chromium oxide and 500° C. for vanadium oxide.

30. A process according to Claim 29, wherein hydrous titanium dioxide is calcined at 700°—1000° C.

31. A process according to any one of Claims 23, 24, 28, 29 or 30, wherein after the deposition on the flakes of titanium or zirconium dioxide by hydrolysis of a titanium or zirconium salt, and before or after any calcination step, a further metal oxide layer or layers are deposited by hydrolysis from acidic solutions of one or more metal salts other than salts of the metal whose oxide forms the greater part or the whole of the first layer, said salts being selected from salts of titanium, zirconium, aluminium, zinc, antimony, tin, iron, copper, nickel, cobalt and chromium.

32. A process for the production of a pigment composition according to Claim 22 substantially as hereinbefore described.

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